

PATENT SPECIFICATION

NO DRAWINGS

849,042



Date of Application and filing Complete Specification: April 22, 1958.

No. 12738/58.

Application made in United States of America on May 20, 1957.

Complete Specification Published: September 21, 1960.

Index at Acceptance:—Classes 1(1), C; and 2(6), P7C(8B:8C:14B:16B:16C), P7D1(A:X), P7T1X.
International Classification:—C08f.

COMPLETE SPECIFICATION

Improvements relating to Polyolefins

We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method of enhancing the cross-linking effectiveness of high energy radiation on polyolefins. More particularly, this invention relates to a method of enhancing the cross-linking effectiveness of high energy radiation on polyethylene and polypropylene which comprises irradiating these polymers in the presence of a chlorobenzene.

Although low molecular weight polypropylenes which are normally liquid at room temperatures have long been known, recently there have been developed polypropylenes which are crystalline solids at room temperature. These unique high molecular weight polypropylenes which have been described in Journal of the American Chemical Society 77, 1708 (1955), "Journal for Polymer Science," XVI, 143 (1955), "Chemical Week" 78, 69-70 (Feb. 4, 1956), "Chemical and Engineering News," Vol. 34, p. 2980, etc., have high melting points and have been prepared as films, fibres, etc. Where the term "polypropylene" is used hereafter in this specification, it refers to these polymers.

When one attempts to cross-link polypropylene with high energy irradiation, unsatisfactory results are usually obtained. Thus, when polypropylene is irradiated in the lower temperature ranges, such as from 25° to 90°C, little cross-linking is effected unless an extremely high dosage is employed and the irradiated polymer produced is unstable to oxygen or air. On the other

[Price 3s. 6d.]

hand, when polypropylene is irradiated at elevated temperature, such as above 125°C, radiation-induced degradation proceeds much faster than cross-linking with the net result that there is a sharp decrease in the cross-linked material formed.

Unexpectedly, it has now been discovered that the cross-linking effectiveness of high energy irradiation can be enhanced by irradiating polypropylene in the presence of a chlorobenzene, whether the irradiation is done at room temperature or at elevated temperature. This result is unexpected since other solvents retard the cross-linking effectiveness of irradiation on polypropylene.

Although the chlorobenzenes have a more marked effect on polypropylene than on polyethylene, they also enhance the cross-linking effectiveness of radiation on polyethylene. As with polypropylene, other solvents only slightly enhance the cross-linking effect or decrease it.

All types of polyethylene are subject to this effect. The treatment of polyethylene with the solvent and the irradiation thereof can be effected in the same manner as with polypropylene. The conditions applicable to polypropylene can also be employed with polyethylene.

In general, the process is carried out by adding a sufficient amount of a chlorobenzene to polyethylene or polypropylene to convert it to a material with enhanced cross-linking ability on irradiation. Any suitable method of adding the chlorobenzene to the polymer can be employed. A convenient method of adding the chlorobenzene to the material is to place the polymer in the solvent to allow the material to become swollen with the chlorobenzene prior to irradiation. After irradiation, the chlorobenzene can be removed from the polymer by any suitable means (*i.e.*, heat, reduced pressure, etc.).

The amount of chlorobenzene in the poly-

Price 25p

mer necessary to effect cross-linking will vary within wide limits depending on the molecular weight of the polymer and the temperature at which it is irradiated. While there appears to be no upper limit to the amount of chlorobenzene which can be used, except as affects ease of operating, there is a minimum amount of chlorobenzene necessary. Although small amounts of chlorobenzene may cause some enhancement in the cross-linking ability of the polymer, at least 10%, but preferably at least 50% of chlorobenzene, based on weight of polymer, should be employed for maximum results. The desired ranges are 10 to 90% preferably 50 to 80%. In addition, chlorobenzene solutions of these polymers may also be irradiated. Although mono- and the isomeric dichlorobenzenes are preferred, other liquid polychlorobenzenes can also be employed.

High voltage accelerating apparatus of the type disclosed in U.S. patent 2,144,518, or of the type described by J. C. Slater in the "Reviews of Modern Physics," Vol. 20, No. 3, pp. 473-518 (July 1948) may be employed for the irradiation.

Uniform treatment of polymeric materials having appreciable thickness can be assured by irradiating them first from one side and then the other or in some cases from both sides simultaneously. In certain instances, it may be desirable to irradiate the polymeric materials in an atmosphere of nitrogen, argon, helium, krypton or xenon, etc., to prevent the damaging effect of any corona which may be present.

To decrease wasteful energy absorption between the point of exit of electrons from the accelerating apparatus and the polymeric materials, a vacuum chamber having thin entrance and exit windows may be inserted in the space.

In general, the energy of the irradiation may range from about 50,000 to 20 million electron volts or higher depending upon materials. The preferable range is 100,000 to 10 million electron volts. Although high energy electron irradiation is preferred since it produces a large amount of easily controllable high energy radiation within a short period of time without rendering the product radioactive, many other sources of high energy irradiation can be used in this invention. Examples of such radiation sources are gamma rays, such as can be obtained from Co^{60} , "burnt" uranium slugs, fission by-products, such as waste solution, separated isotopes, such as Cs^{137} , gaseous fission products liberated from atomic reactions, etc.; other electron sources, such as the betatron, etc., fast or slow neutrons or the mixed neutron and gamma radiation, such as is present in certain atomic reactors;

X-rays; and other miscellaneous sources, such as protons, deuterons, α -particles, fission fragments, such as are available from cyclotrons, etc.

The suitable radiation dose employed in carrying out this invention will of course depend upon the properties desired in the irradiated product and the particular polymer employed. Doses from 1×10^6 rep to 1×10^3 rep, and preferably from 1 to 50×10^6 rep, are employed.

In the following examples all parts are by weight. The apparatus employed was that described in U.S. patent 2,144,518 and was operated with 800 KVP electrons (KVP refers to the peak voltage in kilovolts generated by the inductance coil of the high voltage apparatus during the conducting half cycle which is thus a measure of the energy emerging from the apparatus).

Solubility measurements were employed on the irradiated products to determine the percent. of cross-linked polymer. Solubility measurements as a measure of percentage of cross-linking are based on the phenomenon that when polyethylene or polypropylene is subjected to irradiation, cross-links are formed. At some minimum dose, the number of cross-links is sufficient to form gel particles insoluble in such solvents for these polymers as hot toluene while at higher doses the polymer is sufficiently gelled to resist disintegration in a hot solvent but still yields on swelling some solvent extractable materials.

The effect or irradiation on solubility measurements is determined as follows: A weighed piece of irradiated polymer is immersed in a solvent for the polymer, such as about one litre of toluene, and heated for several hours or more to insure complete extraction. The test piece is then removed from the solvent and dried to constant weight under reduced pressure. Percent. weight loss is equal to
$$\frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100$$
 The percent. of cross linked polymer is equal to 100 minus the percent. weight loss.

In the following examples 5 mil (0.125mm) thick sheets of the polymers were immersed in the solvent until it became saturated with the solvent and the swollen saturated polymer was irradiated under the conditions indicated. The results are shown in the following tables. The untreated polymers were also irradiated as controls.

Polypropylene employed in the examples was obtained from Montecatini of Italy labelled "polipropilene ad alto cristallinata" (hereafter called "alta grade") and "polipropilene ad basa cristallinata" (hereafter called "basa grade").

TABLE I
IRRADIATION OF "BASA GRADE"
POLYPROPYLENE AT 25°C.

Ex.	Radiation Dose (x 10 ⁶ rep.)	Percent. Cross-Linked Polymer	
		Dry	Chlorobenzene
1	10	0	2
2	20	0	32
3	40	0	45
4	50	0	—
5	60	20	65
6	100	33	—
7	150	48	—
8	200	50	—

From Table I it is evident that chlorobenzene markedly enhances the room temperature cross-linking effectiveness of high energy radiation on polypropylene.

- 5 Chlorobenzene can effect at low doses the same amount of cross-linking that can

normally be achieved only at higher doses.

TABLE II
IRRADIATION OF "ALTA GRADE"
POLYPROPYLENE AT 80°C.

Ex.	Solvent	Percent. Cross-Linked Polymer	Radiation Dose (x 10 ⁶ rep.)
9	Chlorobenzene	59	5
10	O-dichlorobenzene	37	5
11	Toluene	—0	5
12	n-Octane	—0	5
13	Dry	—0	20
14	Dry	24	40

From Table II it is evident that the chlorobenzenes enhance the elevated temperature cross-linking effectiveness of high energy radiation on polypropylene. The marked effectiveness of the chlorobenzene on the polymer as compared with other solvents or the dry polymer is shown.

TABLE III

IRRADIATION OF "ALTA GRADE" POLYPROPYLENE
Percent Cross-Linked Polymer

Ex.	Radiation Dose (x 10 ⁶ rep.)	Dry (100°C.)	Chlorobenzene (100°C.)	p-xylene (100°C.)
15	5	0		
16	10	0	73%	0
17	20	24	—	0
		Chlorobenzene (80°C.)	Chlorobenzene (25°C.)	
18	1	6	4	
19	5	71	41	
20	10	80	44	

- 10 Table III demonstrates the enhancement effected by Chlorobenzene over a wide temperature range. It also demonstrates the ineffectiveness of p-xylene in enhancing the cross-linking effectiveness of high energy

radiation

In the following examples polyethylene (DYNH-Bakelite Co.) was irradiated at room temperature. The results are presented in Table IV.

30

TABLE IV
EFFECT OF SOLVENT ON THE 25°C. IRRADIATION CROSS-LINKING
OF POLYETHYLENE
Percent Cross-Linked Polymer

Ex.	Dose (x 10 ⁶ rep.)	Dry	Toluene	CCl ₄	Benzene	n-Octane	Chloro- Benzene	O-Dichloro-Benzene
% absorbed solvent in polymer		0	15	40	11	10	20	23
21	2.5	18						
22	5.0	34	5	15	28	43	28	
23	10.0	53					50	60
24	20.0	67						

- 15 It is seen from the data in Table IV that toluene, benzene and carbon tetrachloride suppress cross-linking while chlorobenzene and o-dichlorobenzene enhance it, although the latter effect is not as pronounced as in polypropylene.

In addition to effectively cross-linking polyethylene and polypropylene, the process of this invention may be applied to the filled polymers. Thus, a large variety of fillers may be used in this invention, the most desirable being those which are capable of

35

enhancing the properties of the polymer. Examples of fillers useful in this invention are carbon blacks, silica xerogels, silica aerogels, fumed silicas, hydrophobic silicas, 5 metal silicates such as calcium silicate, titanium dioxide, zinc oxide, metal carbonates, such as calcium carbonate, magnesium carbonate, aluminas, clays and cominuted glass. As a general rule, it is desirable that 10 the filler have a surface area of about 1 or more square meter per gram but preferably more than about 40 square meters per gram. The amount of filler advantageously present will, of course depend on the particular 15 filler employed and its surface characteristics, etc. may range from 1% to 60% or more based on total weight, with the preferable range being 20—40%.

The products of this invention can be used 20 in those applications where irradiated and unirradiated polyethylene and polypropylene have heretofore been employed except that the irradiated product has the advantage of being a cross-linked polymer with accom- 25 panying improved properties, such as infusibility and enhanced insolubility. Thus, irradiated polyethylene and polypropylene can be used as electrical insulating tapes, as fluid conduits or containers, as filaments or

fibres, as insulating coating on wire, etc. 30

Various modifying agents, such as dyes, pigments, stabilizers, for example, di- α -naphthyl-*p*-phenylene diamine, etc., may be added to the polymer without departing 35 from the scope of the invention. In addition, blends of polyethylene and polypropylene, containing for example from 1—99% parts by weight of polyethylene per 100 parts of both polymers, can be treated according to 40 this invention.

WHAT WE CLAIM IS:

1. The process of cross-linking polyolefins by subjecting the polymer to high energy irradiation of a dose of 1×10^6 to 1×10^8 rep in the presence of a chlorobenzene. 45

2. The process of claim 1 wherein the polyolefin is polypropylene or polyethylene.

3. The process of claim 1 or claim 2 wherein the chlorobenzene is mono- or di-chlorobenzene. 50

4. The process of cross-linking polyolefins by high energy irradiation substantially as described herein.

PHILIP S. ALLAM,
Chartered Patent Agent,
2 and 3, Norfolk Street,
Strand, London, W.C.2.
(Agent for the Applicants).

Leeds: Printed for Her Majesty's Stationery Office, by W. A. Smith (Leeds) Ltd.—1960.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.